SUPPLEMENTARY INFORMATION

Chemical transformation of chiral monolayer-protected gold clusters: Observation of ligand size effects on optical and chiroptical responses

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EDX spectra of fractioned gold cluster compounds $\mathbf{1}_R \text{--} \mathbf{3}_R$

Elemental analysis of the gold cluster samples was conducted using an energy dispersive X-ray (EDX) spectroscopy. Note that, for the analysis, we isolated each fractioned compound as a solid precipitate upon addition of hydrochloric acid. The EDX spectrum was obtained with an EDAX Genesis-2000 system attached to an S-4800 electron microscope. Fig. S1 shows typical EDX spectra of the fractioned gold cluster compounds $(\mathbf{1}_{R}-\mathbf{3}_{R})$ excited by an electron beam at 10 kV. Detection of Si and Al is due to the sample substrate and its support used, respectively. According to the spectra, no X-ray peak of chlorine (Cl: 2.622 keV) was detected for all compounds, which is a clear indication for complete carbamoylation of amino groups in Pen molecules; that is, if unreacted amino groups in Pen ligands remained, we could detect chlorine due to the formation of ammonium salt $(-NH_3^+Cl^-)$. Although there may be some difficulties in obtaining highly accurate quantitative information of low-Z elements (C, N, O),¹ we made practical and reliable determination of the atomic ratios of carbon/sulfur (C/S) and gold/sulfur (Au/S). The most prominent feature is a slight increase in the atomic ratio of C/S from compound 1 to 3; that is, C/S = 8.0 for compound 1, 9.0 for compound 2, and 11.7 for compound 3. The fully carbamovlated Pen ligand has the atomic ratio of C/S = 8. In addition, the atomic ratio of Au/S is almost unchanged for all compounds 1-3 (Au/S = $1.4 \sim 1.6$). The results strongly indicate that additional reaction toward biuret formation should occur for compounds 2 and 3.



Fig. S1. Typical EDX spectra of fractioned gold cluster compounds 1_R - 3_R .



Magnified IR spectra of gold cluster compounds $1_R - 3_R$

Fig. S2. Magnified FT-IR spectra of gold cluster compounds 1_R - 3_R .

Fig. S2 shows magnified FT-IR spectra of gold cluster compounds $\mathbf{1}_{R}$ - $\mathbf{3}_{R}$. This represents a clear spectral difference between these species. Note that such differences could be observed with high reproducibility.

STEM images of compounds 1_R–3_R

FE-STEM images of the fractioned gold cluster compounds $\mathbf{1}_{R}$ - $\mathbf{3}_{R}$ are shown in Fig. S3.



Fig. S3. STEM images of gold cluster compounds $1_R - 3_R$.

Phase transfer experiments for compounds 1_R-3_R

Phase transfer experiment for compounds 1-3 gives us useful information on the surface charge of the ligands of the gold clusters. The experiments were done as follows: (i) Each gel fraction was equally cut and put into the same amount of water, followed by drying completely. Then, 2.0 mL of aqueous NaOH solution (10^{-4} M) was added to prepare the aqueous phase. (ii) 2

mL of toluene containing tetraoctylammonium bromide (TOAB, 9.1×10^{-5} M) was mixed with the water phase and shaken vigorously. Note that we set the TOAB concentration very small (or, the cluster concentration very high) to move the cluster compounds equally to the organic phase. The result is shown in Fig. S4. It should be emphasized that all phase-transferred gold clusters have very similar spectral shape and absorption intensity, meaning that they have identical surface negative charges.



Fig. S4. Absorption spectra of the phase transferred compounds 1_R-3_R in toluene.

Difference between the CD/absorption spectra of compounds 1_s and 3_s (or 1_R and 3_R)

We also calculated the difference (Δ) between the CD (or absorption) spectra of compounds $\mathbf{1}_{s}$ and $\mathbf{3}_{s}$ (or $\mathbf{1}_{R}$ and $\mathbf{3}_{R}$). The results are shown in Fig. S5. The CD difference was very similar to that between $\mathbf{1}_{s}/\mathbf{2}_{s}$ (or $\mathbf{1}_{R}/\mathbf{2}_{R}$). In addition, the first-derivative absorption of $\Delta(\mathbf{1}_{s}-\mathbf{3}_{s})$ was also identical with that of $\mathbf{1}_{s}$. These results strongly indicate that practical contribution from a subtle core size fluctuation to the observed spectral difference should be very small.



Fig. S5. (a) CD signal differences (denoted as a symbol Δ in the figure) between the spectra of $\mathbf{1}_{S}$ (or $\mathbf{1}_{R}$) and $\mathbf{3}_{S}$ (or $\mathbf{3}_{R}$). Red and green curves display the difference spectra for R and S optical isomers, respectively. (b) First-derivative spectra of $\mathbf{1}_{S}$ and $\Delta(\mathbf{1}_{S}-\mathbf{3}_{S})$.

Singlet excited-states of reacted (*R*)-penicillamine with ethyl isocyanate

We utilized the DFT method, employing the B3LYP functional provided by the Gaussian 03 package for the ground-state geometry optimizations of carbamoylated (*R*)-penicillamine and its biuret compound. The standard 6-31G* basis set was used. Excited-state energy calculations were performed using the TD-DFT method at the same level with that for the ground-state calculations. The excited state properties of these compounds are listed in Table 1. It is found that the lowest excitation for the carbamoylated penicillamine or the biuret compound corresponds to the highest occupied molecular orbital (HOMO) \rightarrow lowest unoccupied molecular orbital (LUMO) transition of the COOH or NHCONH group, respectively (see Fig. S6). The excitation energy is thus larger than 5 eV (~250 nm), in good agreement with experimental observation,² so the pure ligand components would not contribute to the wavelength region of 300–400 nm.



Fig. S6. Isodensity plot of the frontier molecular orbitals of (R)-(N-ethylcarbamoyl)penicillamine and its biuret compound computed at the B3LYP/6-31G* level of theory.

Table 1: Excited states of carbamoylated Pen and its biuret compound calculated by the TD-DFT method

	state	main configuration	nature	excitation energy (eV)	excitation energy (nm)	oscillator strength
carbamoylated Pen						
	1st excited state	$0.49 (HOMO \rightarrow LUMO)$	<i>n</i> — <i>л</i> * (СООН)	5.534	224.03	0.0101
	2nd excited state	0.46 (HOMO-1 \rightarrow LUMO)		5.725	216.58	0.0008
biuret compound						
	1st excited state	$0.68 (HOMO \rightarrow LUMO)$	<i>n</i> – <i>π</i> * (NHCONH)	5.263	235.57	0.0062
	2nd excited state	0.58 (HOMO-1 \rightarrow LUMO)		5.478	226.34	0.0287

References

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